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Preparation and Characterization of Single-Crystal



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ABSTRACT

Large (1.5 mm x 1.5 mm x 0.05 mm) single crystals of $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (R = Er, Ho) were grown from nonstoichiometric mixtures of $\text{BaCO}_3\text{-R}_2\text{O}_3\text{-CuO}$. Crystals of $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grown in alumina crucibles have small orthorhombic distortions and are superconducting with resistive T_c (onsets) = 87 K and 80 K respectively. Crystals of $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grown in ZrO_2 crucibles show an onset of diamagnetism at 82 K. A number of experiments were carried out in order to optimize the crystal growth parameters and the results of those experiments are reported herein.

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1. Introduction

Since superconductivity near 30 K was first discovered by Bednorz and Müller,¹ the search for copper oxides which superconduct at even higher temperatures has been remarkably fruitful. Most notably, the discovery of superconductivity at 93 K in a mixed-phase sample in the Y-Ba-Cu-O system² broke the technological barrier of superconductivity above liquid nitrogen temperature (77 K). The phase responsible for this high- T_c superconductivity was quickly identified³ as $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and it was found that the yttrium atoms can be replaced by most of the rare earth elements without affecting the T_c .^{4,5} More recently, high- T_c superconductivity has been discovered in the series

$(\text{BiO})_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$ ($n = 3$; $T_c = 110$ K)⁶ and $(\text{TlO})_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$ ($n = 3$; $T_c = 125$ K).⁷ One common feature of all the new copper oxide high- T_c superconductors is their highly anisotropic structures. Thus, advances in understanding the fundamental properties of these new superconductors depends in part upon obtaining quality single crystals in which the anisotropic physical properties can be measured. At first, single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ large enough for X-ray structure determination (≈ 80 μm) were obtained from solid-state reactions.⁸

Obtaining larger single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was complicated by the fact that $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ does not melt congruently, and is either insoluble or reacts with most common flux materials. Furthermore, once large single crystals are grown, it is difficult to remove the crystals from the melt since all solvents which will dissolve the melt will also decompose the crystals. These problems were overcome by taking advantage of the region of partial melting in the

BaO-CuO-YO_{1.5} phase diagram.⁹ Using nonstoichiometric mixtures of Ba-Y-Cu-O Schneemeyer et al.¹⁰ grew large (4 mm x 4 mm x 0.5 mm) single crystals of YBa₂Cu₃O_{7-δ} which were superconducting at 91 K. The problem of removing the crystals from the melt was simplified since the crystals grow near the top of the melt and can be removed mechanically.

The anisotropic physical properties of single-crystal YBa₂Cu₃O_{7-δ} have been measured by several workers. Iye et al.¹¹ found critical fields typical of quasi-two-dimensional superconductors, while Dinger et al.¹² measuring critical fields and critical currents found anisotropies of 10 or greater. Hikita et al.¹³ were able to grow fairly large (0.5 mm x 0.5 mm x 0.05 mm) crystals of EuBa₂Cu₃O_{7-δ} and found the anisotropy of about 4 in the critical field. Single crystal growth for some of the other rare-earth compounds has also been reported. Noel et al.¹⁴ were able to grow single crystals (0.3 mm x 0.3 mm x 0.1 mm) of TmBa₂Cu₃O_{7-δ}. Katsui et al.¹⁵ were able to grow large (1.5 mm x 1.5 mm x 0.1 mm) single crystals of NdBa₂Cu₃O_{7-δ}; however, they did not report any of the physical properties. Our interest was to extend the single crystal growth techniques for RBa₂Cu₃O_{7-δ} (R = Y, rare earths) to some of the other rare-earth compounds. After an initial scan of the various R-Ba-Cu-O systems, we chose to concentrate on the R = Er and Ho systems. Thus, in the present paper we report the growth of large (1.5 mm x 1.5 mm x 0.05 mm) single crystals of RBa₂Cu₃O_{7-δ} (R = Er, Ho) using a technique similar to that described by Schneemeyer et al.¹⁰ A number of experiments were done in order to optimize the crystal growth parameters (melt composition, crucible material, heating rate, soak time and temperature, cooling rate, and ambient atmosphere) the results of which are reported herein.

2. Experimental

Appropriate amounts of well dried BaCO_3 , R_2O_3 , and CuO were intimately mixed in the ratios listed in Table 1. The best results were obtained when a small amount of melt (ca. 1 g) was used. Using larger amounts of melt often led to difficulty in mechanically removing the crystals from the melt. Crystals were grown in a top-loading crucible furnace in both air and flowing oxygen atmospheres. Crystals grown in a flowing O_2 atmosphere were slightly smaller than those grown in air, however they had higher T_c s. Attempts to improve the physical properties of crystals grown in air by subsequently annealing them in flowing oxygen were unsuccessful. Heating single crystals of $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in alumina boats to 450°C in a flowing oxygen atmosphere led to obvious surface decomposition of the crystals. The surface decomposition problem was overcome by lining the alumina boat with sintered polycrystalline $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$. However, the oxygen anneal still did not improve the physical properties of the crystals. In a typical crystal growth experiment, the reaction mixture was put into the furnace at 450°C , heated to $980\text{--}1030^\circ\text{C}$ at 50°C per hour, and held at $980\text{--}1030^\circ\text{C}$ for 2-5 hours. The melt was then cooled to 880°C at $1 - 5^\circ\text{C}$ per hour, cooled from 880°C to 450°C at 50°C per hour, and held at 450°C for 16 hours. The crucibles used were either McDanel 20 mL high-form high-purity alumina or Alfa 20 mL cylindrical CaO -stabilized ZrO_2 . Crystals tended to grow near the inside rim of the crucible and on the top of the melt. The melt tended to creep out from underneath the crystals, making mechanical removal of the crystals from the melt somewhat easier.

Single-crystal lattice parameters were determined using an Enraf-Nonius CAD-4 diffractometer, with final cell parameters being determined by a least-squares fit of 25 well centered reflections with ($25.3^\circ < 2\theta < 37.4^\circ$). Resistivity measurements were made in the a-b plane of the crystals using the four-probe van der Pauw technique with a measuring current of 1 mA. Electrical contacts to the sample were made with ultrasonically soldered indium, and the temperature was measured using a carbon-glass thermometer which had been calibrated against a silicon diode. As has been noted by previous workers,¹⁰ the contact resistance (200 - 1000 Ω) of our crystals was substantially higher than that obtained for similar contacts to sintered polycrystalline samples (ca. 1 Ω). Magnetic susceptibility measurements were done on a Quantum Designs SQUID magnetometer with the a-b plane of the crystal oriented perpendicular to the direction of the field. The crystals were cooled in zero field to 10 K and the field was then charged to 100 gauss. The shielding data were measured by warming to 160 K and the Meissner data were measured by field cooling down to 10 K.

3. Results and Discussion

A variety of melt compositions and heating programs were studied using both alumina and zirconia crucibles and the results for the $\text{BaCO}_3\text{-Er}_2\text{O}_3\text{-CuO}$ system are summarized in Table 1. Since $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ does not melt congruently and the melts in these experiments are almost certainly complicated mixtures, the optimal growth conditions were found to be a sensitive interplay of all of the many variables. For example, slower heating rates (i.e. 50°C per hour versus 75°C per hour) were

found to yield better quality crystals. The amount of time the melt is held at the high temperature was found to dramatically affect crystal quality. Keeping all other variables constant, crystals grown from melts held at 1000°C for 3 h were of significantly better quality than crystals grown from melts held at 1000°C for 5 h. In general, it seems that since the crystals are metastable under the conditions in which they grow, one should avoid keeping the melt at high temperatures for too long a period of time. Thus, if either the cooling rate is too slow or the soak time at high temperature is too long, one obtains very thin crystals. Apparently, the crystals decompose fastest along the c-direction. Compositions which are rich in copper yield crystals of CuO in addition to crystals of $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The optimal conditions for crystal growth of $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in alumina containers was for the ratio $\text{BaCO}_3:\text{Er}_2\text{O}_3:\text{CuO} = 4:0.7:8$ using the heating program outlined in Table 1. Crystals grown using these conditions were up to 1.5 mm x 1.5 mm x 0.05 mm in size and had well formed faces and sharp corners and edges. Resistivity vs. temperature data for a crystal of $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are shown in Figure 1. The high-temperature region shows a much weaker temperature dependence than is typical for sintered polycrystalline samples and there is a slight upturn to semiconducting behavior before the onset of superconductivity at 87 K. The resistive transition is fairly broad, with $T_c(\text{midpoint}) = 75 \text{ K}$ and $T_c(\text{zero}) = 57 \text{ K}$. The high-temperature behavior as well as the fairly broad transition are probably due to either defects or impurities in the crystal or inhomogeneity of the oxygen distribution such that some regions of the crystal have an oxygen stoichiometry below 6.5 and are therefore not superconducting. Experimentally determined cell parameters for $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($a=3.854(1)\text{\AA}$,

$b=3.861(1)\text{\AA}$, $c=11.664(1)\text{\AA}$) show a much smaller orthorhombic distortion than is typical for polycrystalline samples. This is perhaps due to the microtwinning of the crystals which is evident from examination of peak profiles for high-angle reflections of the $(h00)$ and $(0k0)$ type.

Crystals of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were also grown in alumina crucibles. The optimal conditions for growing single crystals of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are similar to those for $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$. However, in the case of the Ho system the best crystals were obtained from melts containing proportionally less rare earth ($\text{BaCO}_3:\text{Ho}_2\text{O}_3:\text{CuO} = 4:0.5:8$) than in the Er case. The resistivity vs. temperature data for a crystal of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (see Figure 2) are very similar to those for $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (see Figure 1). However, in the case of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ there is a stronger metallic temperature dependence at high temperatures and the resistive transition is sharper ($T_c(\text{onset})=80\text{ K}$, $T_c(\text{midpoint})=70\text{ K}$, $T_c(\text{zero})=66\text{ K}$) than for $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$, but the $T_c(\text{onset})$ is at a slightly lower temperature. The cell parameters for $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ also indicate only a small orthorhombic distortion ($a=3.859(1)\text{\AA}$, $b=3.868(1)\text{\AA}$, $c=11.682(3)\text{\AA}$) with microtwinning evident from examination of the peak profiles of high-angle reflections of the $(h00)$ and $(0k0)$ type.

In order to obtain crystals with better physical properties than those which we grew in alumina crucibles, we also studied the crystal growth of $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in ZrO_2 crucibles. Aluminum from Al_2O_3 crucibles is known to substitute for Cu in the $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ structure resulting in crystals with lower transition temperatures.¹⁶ A comparison of the crystal growth conditions used (see Table 1) in ZrO_2 crucible with those used in Al_2O_3 crucibles shows that the optimal melt compositions are very different in the two types of crucibles. Apparently the small

amount of alumina which is incorporated into the melts in alumina crucibles is enough to dramatically affect the crystal growth and melting behavior of the mixtures. The susceptibility vs. temperature data for an $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystal grown in a ZrO_2 crucible are shown in Figure 3. The Meissner effect is roughly $1/3$ of the shielding effect indicating that some flux is trapped in the crystal, presumable at crystal defects or twin boundaries. The onset of diamagnetism ($T_c=82$ K) occurs at about the same temperature as the resistive transitions in the crystals grown in alumina crucibles. However, since the onset of diamagnetism usually occurs at slightly lower temperature than the resistive onset, the crystals grown in ZrO_2 crucibles are probably of somewhat better quality. Experiments continue in order to further improve the quality of both $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals.

4. Conclusions

Large single crystals of $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($R = \text{Er}, \text{Ho}$) were grown in both alumina and zirconia crucibles. In all cases, the crystals had only a small orthorhombic distortion. This is consistent with the microtwinning which was observed. Crystals of $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have $T_c(\text{onset}) = 87\text{K}$; however, the superconducting transitions are fairly broad. $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystals grown in zirconia crucibles show an onset of diamagnetism at 82 K. It was noted the optimal melt compositions for growing $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystals is very dependent upon the crucible material used.

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TABLE CAPTION

Table 1. Experimental parameters for growth of single-crystal
 $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

FIGURE CAPTIONS

- Figure 1. Resistivity vs. temperature data for a single crystal of $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grown in an Al_2O_3 crucible.
- Figure 2. Resistivity vs. temperature data for a single crystal of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grown in an Al_2O_3 crucible.
- Figure 3. Susceptibility vs. temperature data for a single crystal of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grown in a ZrO_2 crucible.

TABLE 1

| BaCO ₃ :Er ₂ O ₃ :CuO | Heating (°C/h) | Soak | Cooling (°C/h) | Crucible | Comment |
|--|-------------------|--------------|-------------------|--------------------------------|-------------------------|
| 4:1.0:9 | 75 | 1030°C, 4 h | 1 | Al ₂ O ₃ | Large, thin crystals |
| 4:0.5:8 | 50 | 1000°C, 3 h | 4 | Al ₂ O ₃ | Few, large crystals |
| 4:0.6:8 | 50 | 1000°C, 3 h | 4 | Al ₂ O ₃ | Good morphology |
| 4:0.7:8 | 50 | 1000°C, 3 h | 4 | Al ₂ O ₃ | Many, large crystals |
| 4:0.5:10 | 50 | 1000°C, 3 h | 4 | Al ₂ O ₃ | CuO crystals |
| 4:0.5:10 | 50 | 1030°C, 3 h | 5 | ZrO ₂ | little melting |
| 4:0.5:14 | 50 | 1000°C, 3 h | 5 | ZrO ₂ | Large, thin crystals |
| 4:0.5:14 | 50 | 1000°C, 24 h | 4 | ZrO ₂ | Few crystals |
| 4:0.7:16 | 50 | 1025°C, 3 h | 5 | ZrO ₂ | CuO crystals |

FIGURE 1.

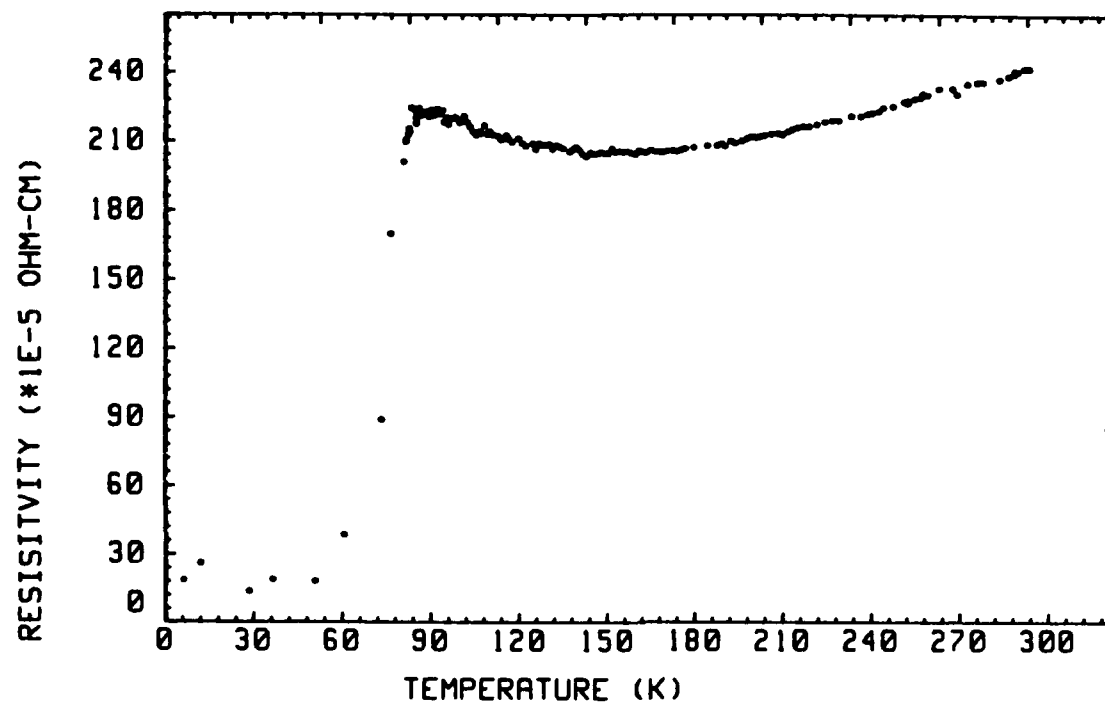


FIGURE 2.

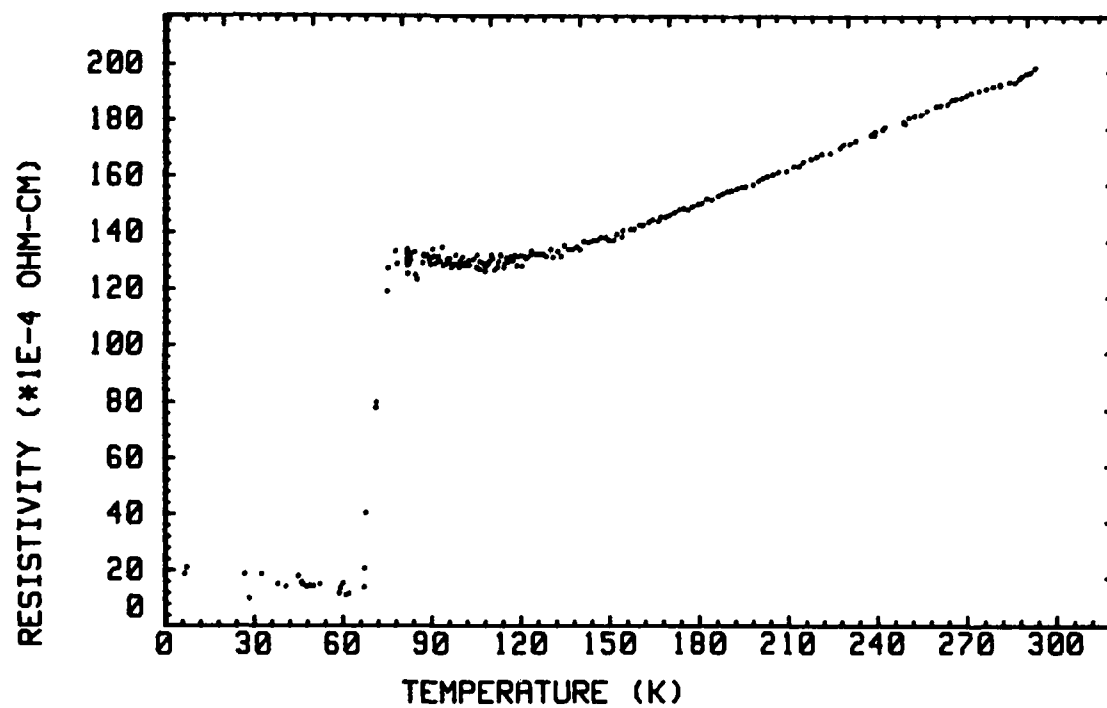


FIGURE 3.

